Pressure of ideal gas from the kinetic theory I

Molecule = point mass

N molecules of masses m_i, $i = 1, .., N$, in a cube of edge L

Velocity of molecule i is $\vec{v}_i = (v_{i,x}, v_{i,y}, v_{i,z})$

After elastic reflection: $v_{i,x} \rightarrow -v_{i,x}$

A molecule hits the same wall again after time $t = 2L/v_{i,x}$

Force = change of momentum in a time unit

Momentum $\vec{P} = m\vec{v}$

Change of momentum $= \Delta P_x = 2m_i v_{i,x}$

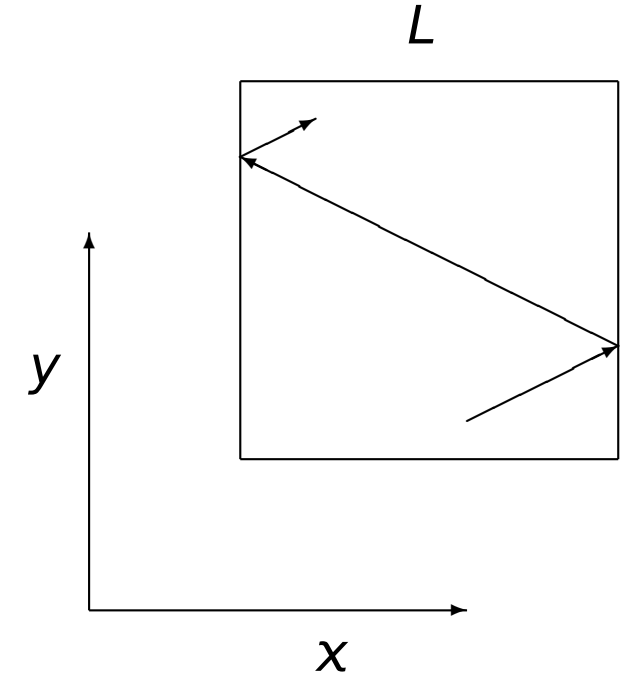**Averaged** force caused by impacts of one molecule:

$$F_{i,x} = \frac{\Delta P_x}{t} = \frac{2m_i v_{i,x}}{2L/v_{i,x}} = \frac{m_i v_{i,x}^2}{L}$$

Pressure = force of all N molecules, divided by the area

$$p = \frac{\sum_{i=1}^{N} F_{i,x}}{L^2} = \frac{\sum_{i=1}^{N} m_i v_{i,x}^2}{L^3}$$

Kinetic energy of one molecule

$$\frac{1}{2} m_i |\vec{v}_i|^2 \equiv \frac{1}{2} m_i v_i^2 = \frac{1}{2} m_i (v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2)$$

Pressure of ideal gas from the kinetic theory II

Kinetic energy of gas = internal energy (monoatomic gas)

$$E_{kin} = \frac{1}{2}\sum_{i=1}^{N} m_i v_i^2 = \frac{3}{2}\sum_{i=1}^{N} m_i v_{i,x}^2$$

$\Rightarrow$

$$p = \frac{\sum_{i=1}^{N} m_i v_{i,x}^2}{L^3} = \frac{2}{3}\frac{E_{kin}}{V}$$

In other words

$$pV = \frac{2}{3}E_{kin} \overset{!}{=} nRT$$

Temperature is a measure of kinetic energy

Assumptions:

🟣 Pressure is a result of **averaged** impacts of molecules

🟣 We used the **classical mechanics**

⚪ Quantum effects at low T: $p < nRT/V$ for bosons, $p > nRT/V$ for fermions

Equation of state:

$$pV = nRT = Nk_\mathrm{B}T$$

$$N = nN_\mathrm{A}$$

also "thermal equation of state"

Energy

$$U \equiv E_\mathrm{kin} = \frac{3n}{2}RT = \frac{3N}{2}k_\mathrm{B}T$$

"caloric equation of state" / "internal energy"

where the Boltzmann constant is

$$k_\mathrm{B} = \frac{R}{N_\mathrm{A}}$$

Defined since May 5, 2019:
$k_\mathrm{B} = R/N_\mathrm{A} = 1.380649 \times 10^{-23}\,\mathrm{J\,K^{-1}}$,
$N_\mathrm{A} = 6.02214076 \times 10^{23}\,\mathrm{mol^{-1}}$,
hence **exactly**
$R = 8.31446261815324\,\mathrm{J\,mol^{-1}\,K^{-1}}$
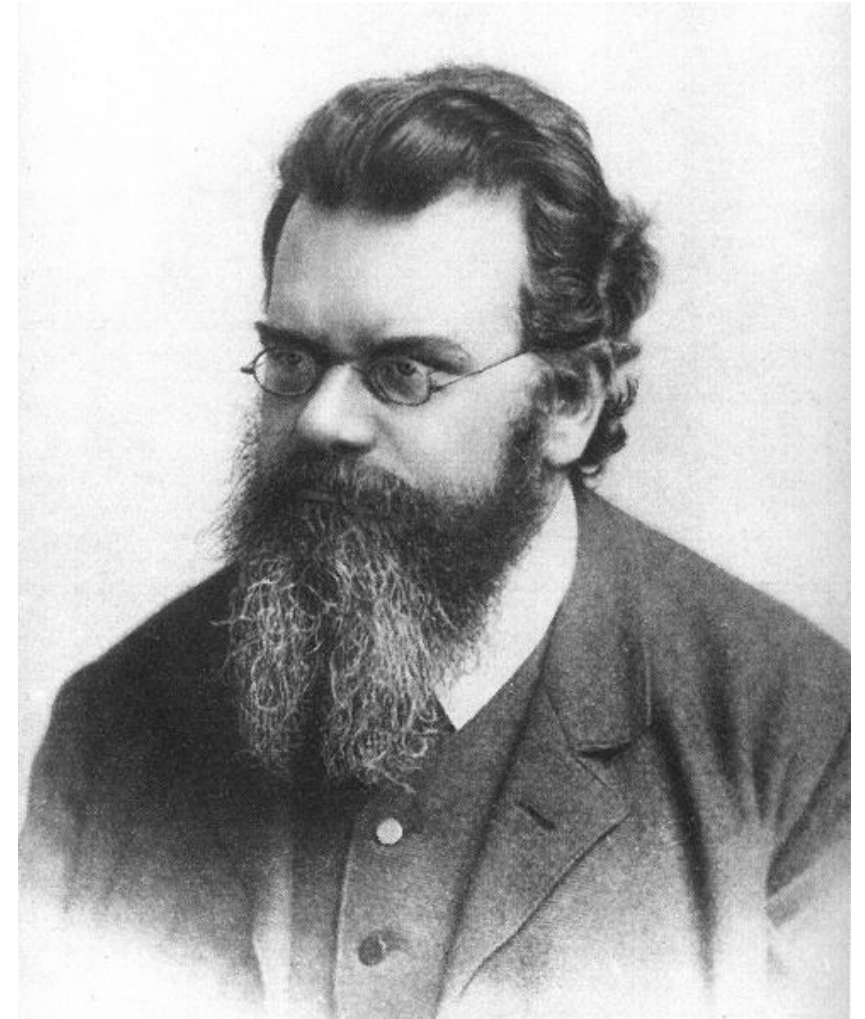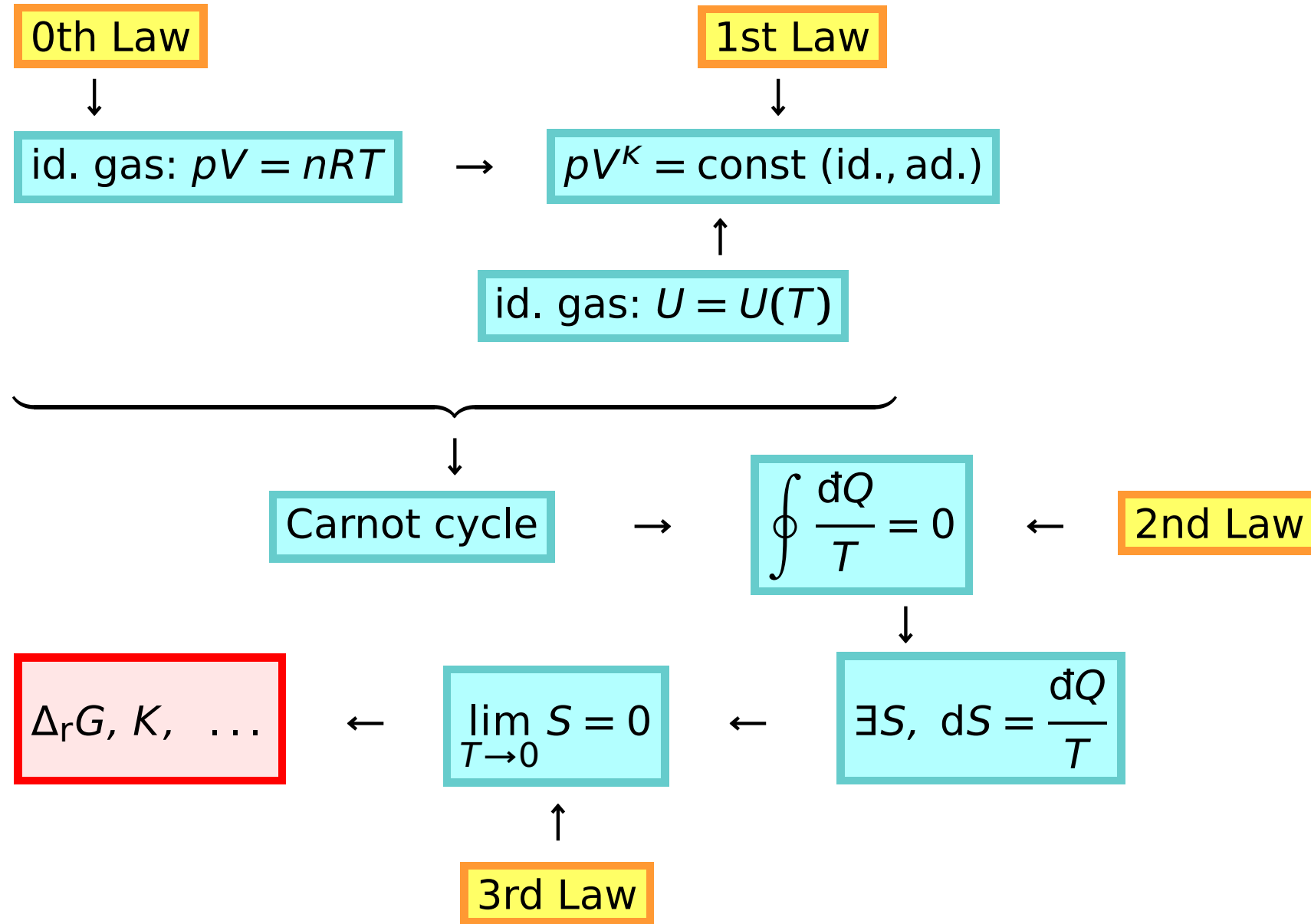

Ludwig Eduard Boltzmann (1844–1906)
credit: scienceworld.wolfram.com/biography/Boltzmann.html

(both equations of state are needed to define entropy)

0th Law

1st Law

↓

↓

id. gas: $pV = nRT$

→

$pV^K = \text{const (id., ad.)}$

↑

id. gas: $U = U(T)$

↓

Carnot cycle

→

$\oint \dfrac{đQ}{T} = 0$

←

2nd Law

↓

$\Delta_r G,\ K,\ \ldots$

←

$\lim\limits_{T \to 0} S = 0$

←

$\exists S,\ dS = \dfrac{đQ}{T}$

↑

3rd Law

Expression E_{kin} is composed of $f = 3N$ terms of the form $\frac{1}{2}m_i v_{i,k}^2$, where $k \in \{x, y, z\}$.

$$pV = Nk_BT = \frac{f}{3}k_BT = \frac{2}{3}E_{kin}$$

$f =$ **number of mechanical degrees of freedom**.
Average energy contribution per one degree of freedom:

$$\frac{E_{kin}}{f} = \frac{1}{2}k_BT$$

Generalization: any quadratic function in the Hamiltonian

Heat capacity in molar units ($N = N_A$, $f = 3N_A$):

degrees of freedom per molecule

$$C_{Vm} = \left(\frac{\partial U_m}{\partial T}\right)_V = \left(\frac{\partial E_{kin,m}}{\partial T}\right)_V = \frac{\frac{1}{2}fk_BT}{N_AT} = \frac{3}{2}R$$

Extension:

- Linear molecules: + 2 rotations, $C_{Vm} = \frac{5}{2}R$ (but: hydrogen)
- Nonlinear molecules: + 3 rotations, $C_{Vm} = 3R$
- (Vibrations classically: + 2 for each (incl. E_{pot}) – imprecise!)

Calculate $C_{p\mathrm{m}}$ for nitrogen and water vapor.

N_2: $C_{V\mathrm{m}} = \frac{5}{2}R$, $C_{p\mathrm{m}} = C_{V\mathrm{m}} + R = 3.5R = 29.10\,\mathrm{J\,K^{-1}\,mol^{-1}}$

H_2O: $C_{V\mathrm{m}} = \frac{6}{2}R$, $C_{p\mathrm{m}} = C_{V\mathrm{m}} + R = 4R = 33.26\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Experiment: N_2 (300 K): $29.12\,\mathrm{J\,K^{-1}\,mol^{-1}}$

H_2O (500 K): $35.22\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Isobaric heat capacity of water vapor → → →
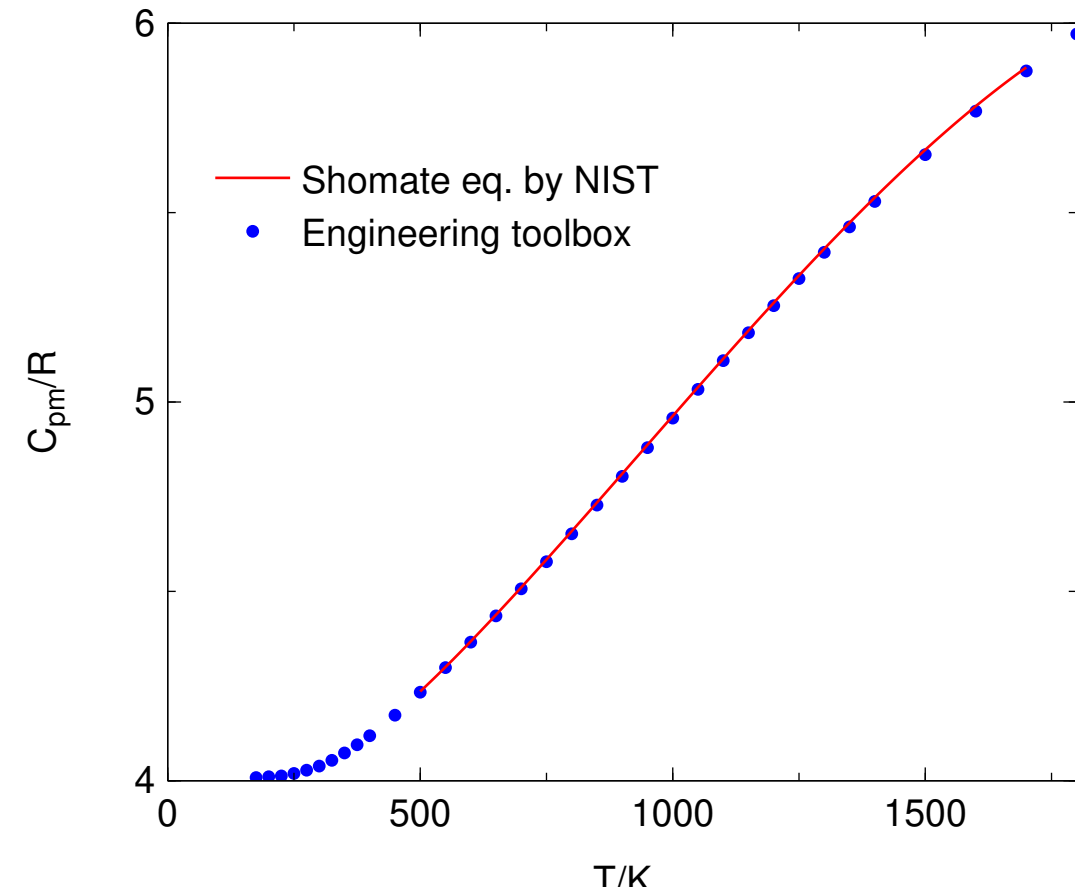
- **microstate** (state, configuration) = instantaneous "snapshot" at given time

  quantum description: state = eigenstate (wave function ψ)

  classical description: state = positions and velocities* of all particles

  at given time, $\psi = (\vec{r}_1, \ldots, \vec{r}_N, \vec{v}_1 \ldots, \vec{v}_N)$

- **macrostate** = averaged action of all microstates

- **ensemble** = set of all microstates with known probabilities $\boldsymbol{\pi(\psi)}$

- **trajectory** = record of a time development of a microstate

microstate   macrostate   ensemble   trajectory
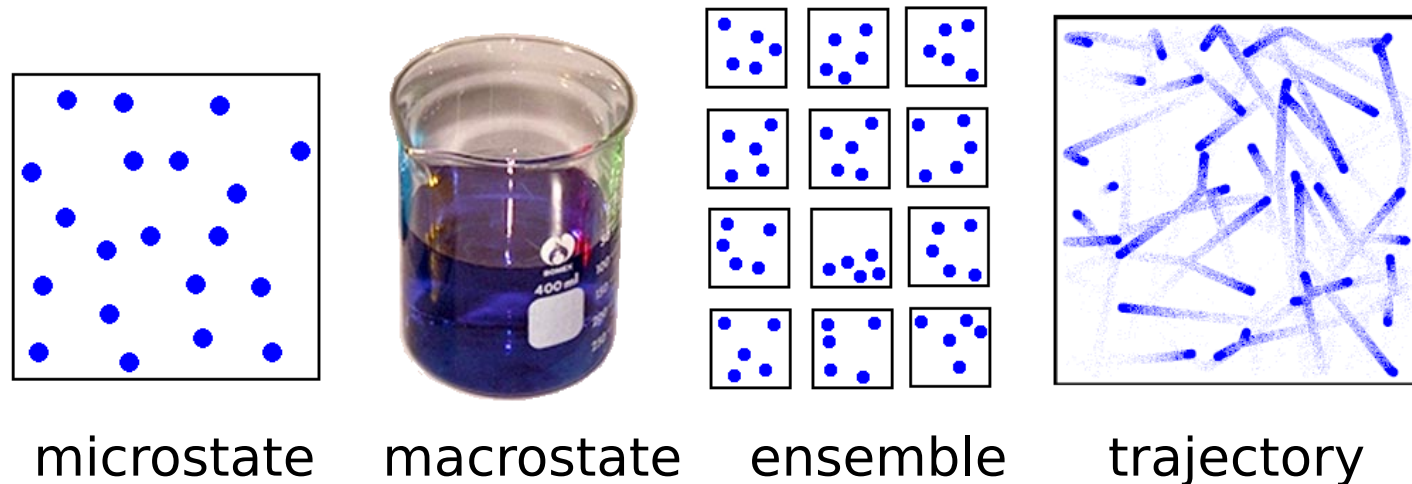
*in fact, momenta – more later. There are ∞ states, hence we work with their probability density $\rho(\psi) \equiv \rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)$.

Microcanonical ensemble and ergodic hypothesis

Microcanonical ensemble = ensemble of microstates in an isolated system (which has developed in time for a long time)

Also denoted as **NVE** ($N = $ const, $V = $ const, $E = $ const)

for me:
e NVE ensemble
r smaller balls
c trajectory

⬤ **Ergodic hypothesis** (quantum): $\pi(\psi_i) = \text{const} = \frac{1}{W}$ ($W = $ # of states)

⬤ **Ergodic hypothesis** (classical):
   trajectory covers the space† with uniform probability

In other words:

Time average (over a trajectory)

$$= \langle X \rangle_t = \lim_{t \to \infty} \frac{1}{t} \int_0^t X(t)\, \mathrm{d}t$$

= ensemble average

$$= \langle X \rangle = \frac{1}{W} \sum_\psi X(\psi)$$

for any quantity $X = X(\psi)$, where $\psi = \psi(t)$

†namely: the phase state of $\{(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1 \ldots, \vec{p}_N)\}$

Mean value in the microcanonical ensemble

$$\langle X \rangle = \frac{\sum_\psi X(\psi)}{W}$$

Example. You win \$5 if you throw ⚅ on a dice, you loose \$1 if you throw anything else. What is your mean (expected) win in this game?

⚀ ⚁ ⚂ ⚃ ⚄ ⚅

$$\langle \text{win} \rangle = \frac{-1-1-1-1-1+5}{6} = 0$$

Whole thermodynamics can be built on the top of the microcanonical ensemble.
But for $T = \text{const}$ it is much easier.

We want T = const: Canonical ensemble

NVT (N = const, V = const, T = const)

Ergodic hypothesis: $\pmb{\pi}(\psi) = \pmb{\pi}(\mathcal{E}(\psi))$
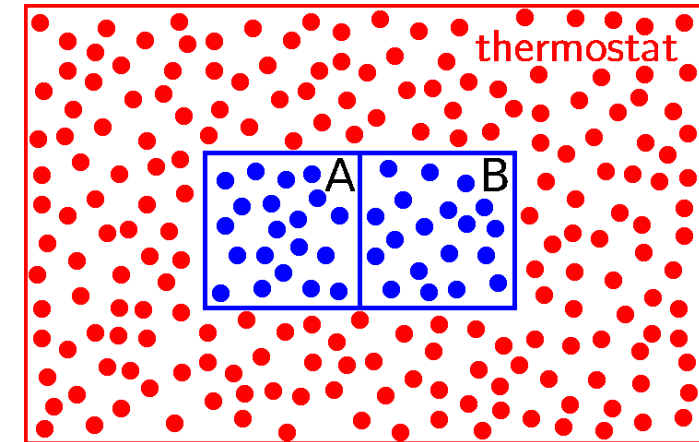
$E_A + E_B = E_{A+B}$ (do not interact)

$\pmb{\pi}(E)$ = probability of any state
      with energy E

E_3	ψ_9	ψ_{10}	ψ_{11}	ψ_{12}	ψ_{13}	ψ_{14}	ψ_{15}
E_2	ψ_4	ψ_5	ψ_6	ψ_7	ψ_8		
E_1	ψ_1	ψ_2	ψ_3				
E_0	ψ_0						

$$\pmb{\pi}(E_A) \cdot \pmb{\pi}(E_B) = \pmb{\pi}(E_{A+B}) = \pmb{\pi}(E_A + E_B)$$

$$\Rightarrow \pmb{\pi}(E) = \text{const}^E = \exp(\alpha_i - \beta E)$$

🟣 0th Law $\Rightarrow \beta$ is empirical temperature

🟣 α_i is system-dependent normalizing const. so that $\sum_\psi \pmb{\pi}(\psi) = 1$

Determining β: monoatomic perfect gas, per 1 atom $U_1 = \frac{3}{2}k_B T$

$$\langle U_1 \rangle = \frac{\sum_\psi \mathcal{E}(\psi)\pmb{\pi}(\mathcal{E}(\psi))}{\sum_\psi \pmb{\pi}(\mathcal{E}(\psi))} = \frac{\int \frac{1}{2}m\vec{v}^2 \pmb{\pi}(\frac{1}{2}m\vec{v}^2)\,d\vec{v}}{\int \pmb{\pi}(\frac{1}{2}m\vec{v}^2)\,d\vec{v}}$$

Evaluation gives: $\langle U_1 \rangle = \frac{3}{2}\frac{1}{\beta}$ $\Rightarrow$ $\beta = \frac{1}{k_B T}$

$$\langle U_1 \rangle = \frac{\int_{R^3} \frac{1}{2} m \vec{v}^2 \pi(\frac{1}{2} m \vec{v}^2) \, d\vec{v}}{\int_{R^3} \pi(\frac{1}{2} m \vec{v}^2) \, d\vec{v}}$$

$$= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) \, e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}$$

$$= 3 \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{2} m v_x^2 \, e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}$$

$$= 3 \boxed{\frac{\int_{-\infty}^{\infty} \frac{1}{2} m v_x^2 \, e^{-\frac{1}{2}\beta m v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x}} = 3 \frac{\frac{1}{2} m \frac{1}{2\frac{1}{2}\beta m} \sqrt{\frac{\pi}{\frac{1}{2}\beta m}}}{\sqrt{\frac{\pi}{\frac{1}{2}\beta m}}} = \frac{3}{2} \frac{1}{\beta}$$

We have used the **Gauss integral**: $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ (where $a = \frac{1}{2}\beta m$)

and its derivate by parameter a:

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = -\frac{d}{da} \int_{-\infty}^{\infty} e^{-ax^2} dx = -\frac{d}{da} \sqrt{\frac{\pi}{a}} = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

$$\frac{\int_{-\infty}^{\infty} \frac{1}{2}mv_x^2\, e^{-\frac{1}{2}\beta m v_x^2}\, dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2}\, dv_x} = \frac{1}{2\beta}$$

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C Maple Input   Monospaced   12   B I U

```
> int(1/2*m*(vx^2)*exp(-beta*m*vx^2/2), vx=-infinity..infinity) /
  int(exp(-1/2*beta*m*(vx^2)), vx=-infinity..infinity)
  assuming m>0,beta>0;
```

$$\frac{1}{2\,\beta}$$

>

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Mean value in the canonical ensemble

Generalization of the mean value (= expectation value):

$$\langle X \rangle = \sum_\psi X(\psi)\pi(\mathcal{E}(\psi)) = \sum_\psi X(\psi)e^{\alpha - \beta\mathcal{E}(\psi)} = \frac{\sum_\psi X(\psi)e^{-\beta\mathcal{E}(\psi)}}{\sum_\psi e^{-\beta\mathcal{E}(\psi)}}$$

Boltzmann factor: $e^{-\mathcal{E}(\psi)/k_B T}$

Example. You win \$5 if you throw ⚅ on a dice, you loose \$1 if you throw anything else. However, you have drilled a small lead weight under ⚀ (opposite to ⚅) so that the probabilities are $\pi(⚅) = 0.2$ and $\pi(⚀) = \pi(⚁) = \pi(⚂) = \pi(⚃) = \pi(⚄) = 0.16$. What is your mean (expected) win in this game?

Note: $5 \times 0.16 + 0.2 = 1$ (normalized)

$$\qquad\qquad ⚀ \qquad\quad ⚁ \qquad\quad ⚂ \qquad\quad ⚃ \qquad\quad ⚄ \qquad\quad ⚅$$
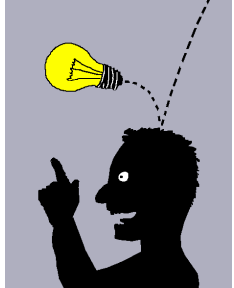
$$\langle \text{win} \rangle = -1 \cdot 0.16 - 1 \cdot 0.16 - 1 \cdot 0.16 - 1 \cdot 0.16 - 1 \cdot 0.16 + 5 \cdot 0.2 = 0.2$$

... or the first half of statistical thermodynamics.

Probability of finding a state with energy $\mathcal{E}$ is proportional to

$$\pi(\mathcal{E}) = \text{const} \cdot \exp\left[-\frac{\mathcal{E}(\psi)}{k_B T}\right] = \text{const} \cdot \exp\left(-\frac{E_m}{RT}\right)$$

Examples:

- a reacting system can overcome the activation energy E^* with probability $\sim \exp\left(-\frac{E^*}{RT}\right) \Rightarrow$ Arrhenius formula

$$k = A\exp\left(-\frac{E^*}{RT}\right)$$

- the energy needed for transfering a molecule from liquid to gas is $\Delta_{vap}H_m$ (per mole), probability of finding a molecule in vapor is proportional to $\sim \exp\left(-\frac{\Delta_{vap}H_m}{RT}\right) \Rightarrow$ Clausius–Clapeyron equation (integrated)

$$p = p_0\exp\left[-\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] = \text{const} \cdot \exp\left(-\frac{\Delta_{vap}H_m}{RT}\right)$$

Case study: Barometric formula

...Boltzmann probability once again

Potential energy of a molecule in a homogeneous gravitational field $U_{\mathrm{pot}} = mgh$.
Probability of finding a molecule in height h:

$$\pi \propto \exp\left(-\frac{U_{\mathrm{pot}}}{k_{\mathrm{B}}T}\right) = \exp\left(-\frac{mgh}{k_{\mathrm{B}}T}\right) = \exp\left(-\frac{Mgh}{RT}\right)$$

Probability $\propto$ density $\propto$ pressure:

$$p = p_0 \exp\left(-\frac{Mgh}{RT}\right)$$

The same formula can be derived from the condition of mechanical equilibrium + ideal gas equation of state

$$\mathrm{d}p = -\mathrm{d}h\rho g = -\mathrm{d}h\frac{Mp}{RT}g$$

$$\int_{p_0}^{p} \frac{\mathrm{d}p}{p} = -\int_{0}^{h} \mathrm{d}h\frac{Mg}{RT} \quad \Rightarrow \quad \ln\frac{p}{p_0} = -h\frac{Mg}{RT}$$

Boltzmann probability

Example Energy of the gauche conformation of butane is by $\Delta E = 0.9$ kcal/mol higher than anti. Calculate the population of molecules which are in the gauche state at temperature 272.6 K (boiling point). (1 cal = 4.184 J).

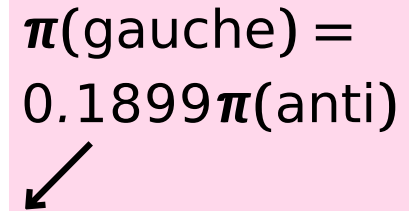**Solution:** There are two gauche states and one anti state!

$$\pi(\text{gauche}+) = \pi(\text{gauche}-)$$

$$\pi(\text{gauche}) : \pi(\text{anti}) = \exp[-\Delta E/RT] = 0.1899$$

$$\pi(\text{gauche}) = 0.1899\,\pi(\text{anti})$$

$$2\,\pi(\text{gauche}) + \pi(\text{anti}) = 1$$

$$\pi(\text{anti}) = \frac{1}{2\exp[-\Delta E/RT] + 1} = \frac{1}{2 \times 0.1899 + 1} = 0.725$$

$$2\,\pi(\text{gauche}) = \frac{2\exp[-\Delta E/RT]}{2\exp[-\Delta E/RT] + 1} = \frac{2 \times 0.1899}{2 \times 0.1899 + 1} = \underline{0.275}$$

Note: we assumed that both minima are well separated and their shapes are identical. Better formula would be with ΔG instead of ΔE. ΔG includes the factor of 2 as well as vibrations which will be a little different in both states. In fact, we solve the equilibrium:

$$\text{anti} \rightarrow \text{gauche}, \quad K = \exp[-\Delta G/RT]$$

Internal energy

$$U = \sum_{\psi} \mathcal{E}(\psi)\boldsymbol{\pi}(\psi)$$

Its small change is

$$dU = \sum_{\psi} \boldsymbol{\pi}(\psi) \cdot d\mathcal{E}(\psi) + \sum_{\psi} d\boldsymbol{\pi}(\psi) \cdot \mathcal{E}(\psi)$$

$d\mathcal{E}(\psi)$: energy level changed
$d\boldsymbol{\pi}(\psi)$: probability of state ψ changed

1st + 2nd Law:

$$dU = -p\,dV + T\,dS$$

- $-p\,dV$: A "piston" moved by dx. Change in energy $= d\mathcal{E}(\psi)$ **= mechanical work** $= -F\,dx = -F/\mathcal{A} \cdot d(\mathcal{A}x) = -p(\psi)\,dV$
  $p(\psi) =$ "pressure of state ψ", pressure $= p = \sum_{\psi} \boldsymbol{\pi}(\psi)p(\psi)$.

- $T\,dS$: Change $\boldsymbol{\pi}(\psi)\,[V]$ = change of the population of states with varying energies **= heat**

Boltzmann equation for entropy

...or the 2nd half of the statistical thermodynamics

$$\pi(\mathcal{E}(\psi)) = \exp(\alpha_i - \beta\mathcal{E}(\psi)) \quad \overset{\beta=1/k_BT}{\Rightarrow} \quad \mathcal{E}(\psi) = k_BT[\alpha_i - \ln\pi(\psi)], \qquad \sum_\psi d\pi(\psi) = 0$$

$$\sum_\psi d\pi(\psi)\mathcal{E}(\psi) = \sum_\psi d\pi(\psi)k_BT[\alpha_i - \ln\pi(\psi)] = -k_BT\sum_\psi d\pi(\psi)\cdot\ln\pi(\psi)$$

$$= -k_BT\,d\left[\sum_\psi \pi(\psi)\ln\pi(\psi)\right]$$

On comparing with $T\,dS$:

$$S = -k_B\sum_\psi \pi(\psi)\ln\pi(\psi)$$

Microcanonical ensemble: $\pi(\psi) = \begin{cases} 1/W & \text{for } E = \mathcal{E}(\psi) \\ 0 & \text{for } E \neq \mathcal{E}(\psi) \end{cases}$

Boltzmann equation: $\boxed{S = k_B\ln W}$

Property: $S_{1+2} = S_1 + S_2 = k_B\ln(W_1W_2) = k_B\ln(W_{1+2})$

credit: schneider.ncifcrf.gov/ images/boltzmann/ boltzmann-tomb-8.html

If we consider transitions between states, we can derive $\frac{dS}{dt} \geq 0$ (H-theorem)

Energies of neighbors: $\bullet\!-\!\bullet = \bullet\!-\!\bullet = \bullet\!-\!\bullet$

All configurations have the same energy

Mix N_1 molecules of 1 + N_2 molecules of 2:

$$W = \binom{N}{N_1} = \frac{N!}{N_1! N_2!}$$

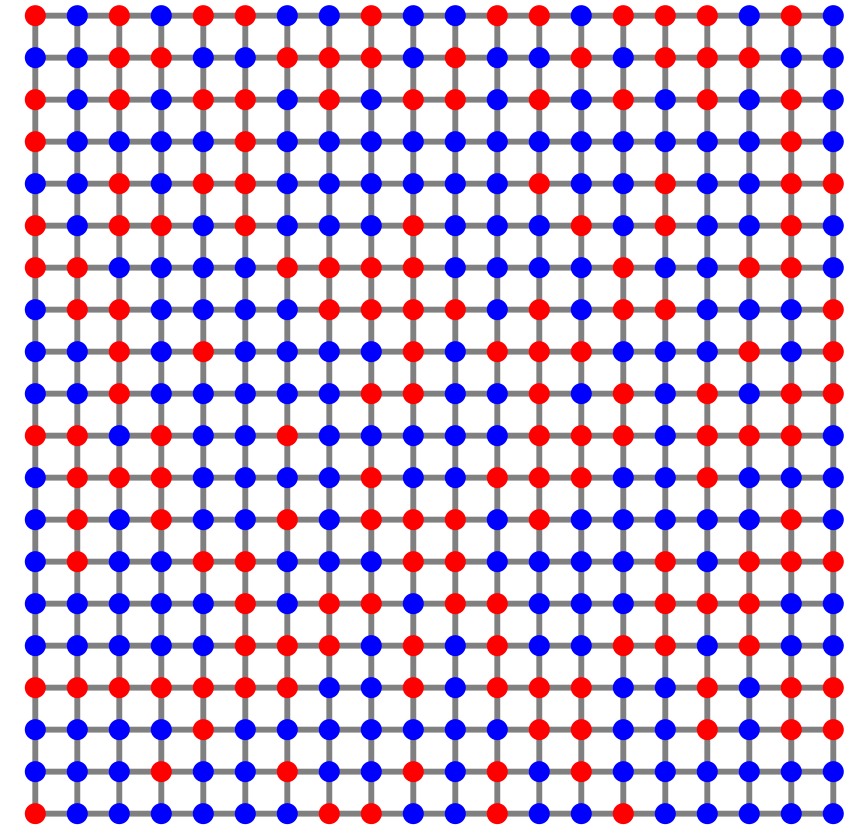$$S = k_B \ln W \approx -k_B \left(N_1 \ln \frac{N_1}{N} + N_2 \ln \frac{N_2}{N} \right)$$

$$S_m = -R\left(x_1 \ln x_1 + x_2 \ln x_2 \right)$$

cf. $S = -k_B \sum_\psi \pi(\psi) \ln \pi(\psi)$

We used the Stirling formula, $\ln N! \approx N \ln N - N$:

$$\ln N! = \sum_{i=1}^{N} \ln i \approx \int_0^N \ln x \, dx \overset{\text{by parts}}{=} [x \ln x - x]_0^N = N \ln N - N$$

More accurately: $\ln N! \overset{\text{asympt.}}{=} N \ln N - N + \ln \sqrt{2\pi N} + \frac{1}{12N} - \frac{1}{360N^3} + \frac{1}{1260N^5} - + \cdots$

Example: Residual entropy of crystals at $T \to 0$

Crystal: 1 microstate $\Rightarrow S = k_B \ln 1 = 0$ (3rd Law)

3rd Law violation: CO, N_2O, H_2O.
Not in the true equilibrium, but "frozen"
because of high barriers

Example 1: Entropy of a crystal of CO at 0 K

$$S_m = k_B \ln 2^{N_A} = R \ln 2$$

Example 2: Entropy of ice at 0 K

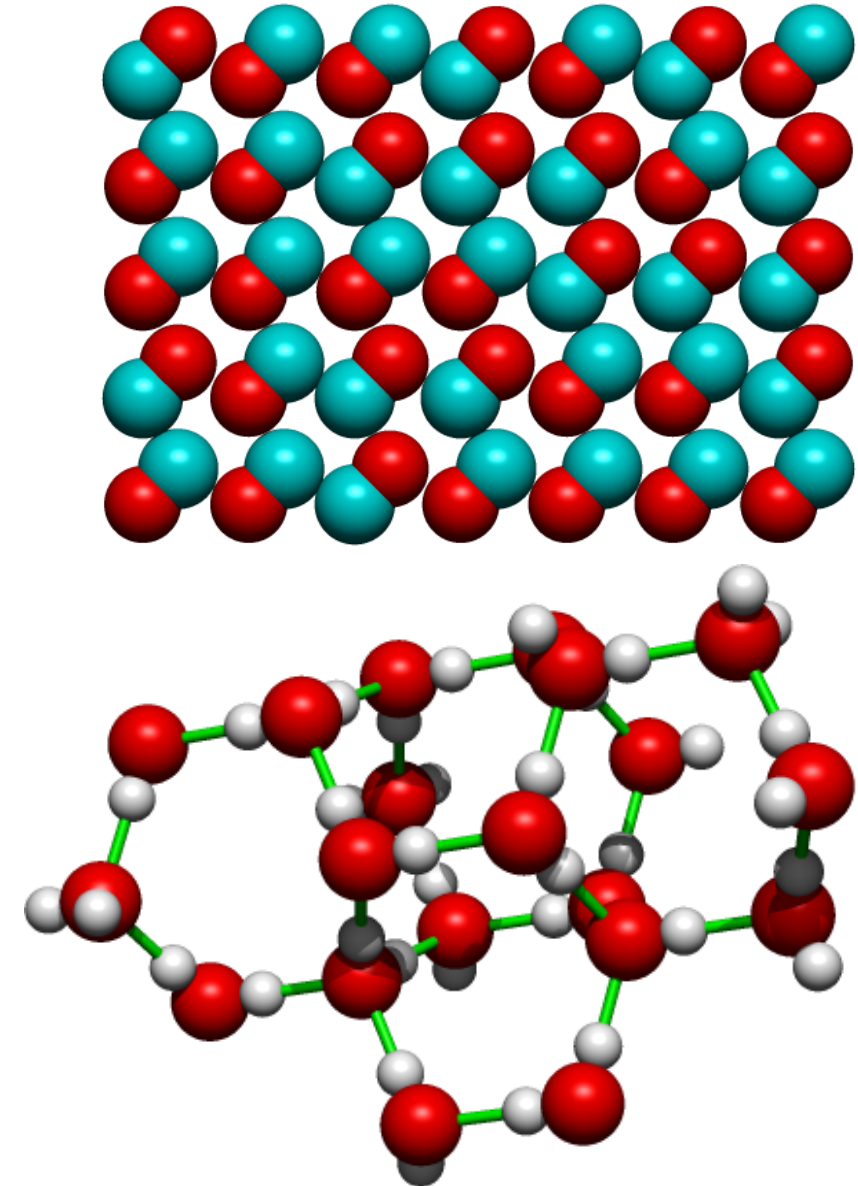$$S_m = k_B \ln 1.507^{N_A} = 3.41 \, J \, K^{-1} \, mol^{-1}$$

Pauling's derivation:

- $6 = \binom{4}{2}$ orientations of a water molecule

- then an H-bond is wrong with prob.$= \frac{1}{2}$

- $2N_A$ bonds in a mole

- $\Rightarrow S_m = k_B \ln \left(\frac{6^{N_A}}{2^{2N_A}} \right) = 3.37 \, J \, K^{-1} \, mol^{-1}$

Example: Information entropy of DNA

Assuming random and equal distribution of base pairs.

Per one base pair: $S = k_\text{B} \ln 4$, per mole: $S_m = R \ln 4$.

Corresponding Gibbs energy (at 37 °C):

$$\Delta G_\text{m} = -RT \ln 4 = -3.6 \, \text{kJ} \, \text{mol}^{-1}$$

To be compared to: ATP → ADP
– standard: $\Delta_\text{r} G_\text{m}^{\ominus} = -31 \, \text{kJ} \, \text{mol}^{-1}$
– in usual conditions in a cell: $\Delta_\text{r} G_\text{m} = -57 \, \text{kJ} \, \text{mol}^{-1}$

$\alpha = ?$

$$\boldsymbol{\pi}(\psi) = \exp[\alpha - \beta \mathcal{E}(\psi)]$$

$$\sum \boldsymbol{\pi}(\psi) = 1 \;\Rightarrow\; \sum \mathrm{d}\boldsymbol{\pi}(\psi) = 0$$

$$S = -k_\mathrm{B} \sum_\psi \boldsymbol{\pi}(\psi) \ln \boldsymbol{\pi}(\psi) = -k_\mathrm{B} \sum_\psi \boldsymbol{\pi}(\psi)[\alpha - \beta \mathcal{E}(\psi)] = -\left(k_\mathrm{B}\alpha - \frac{U}{T}\right)$$

$$\Rightarrow \quad \alpha = \frac{U - TS}{k_\mathrm{B}T} = \frac{F}{k_\mathrm{B}T} \quad \Rightarrow \quad F = -k_\mathrm{B}T \ln\left[\sum_\psi \mathrm{e}^{-\beta \mathcal{E}(\psi)}\right]$$

$[\ldots]$ = **canonical partition function** = **statistical sum** (Q or Z)

Interpretation: number of "accessible" states (low-energy states are easily accessible, high-energy states are not)

From the Helmholtz energy F we can obtain all quantities:

$$\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T$$

$$p = -\frac{\partial F}{\partial V}$$

$$S = -\frac{\partial F}{\partial T}$$

$$\begin{aligned} U &= F + TS \\ H &= U + pV \\ G &= F + pV \end{aligned}$$

Hamilton formalism: positions of atoms $= \vec{r}_i$, momenta $= \vec{p}_i$.

$$\mathcal{E} = \mathcal{H} = E_{\text{pot}} + E_{\text{kin}}, \quad E_{\text{pot}} = U(\vec{r}_1, \ldots, \vec{r}_N), \quad E_{\text{kin}} = \sum_i \frac{\vec{p}_i^2}{2m}$$

Sum over states replaced by integrals (clasical mechanics needed):

$$Z = \sum_\psi e^{-\beta\mathcal{E}(\psi)} = \frac{1}{N! h^{3N}} \int \exp[-\beta\mathcal{H}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)] \, d\vec{r}_1 \cdots d\vec{p}_N$$

where $h = 2\pi\hbar =$ Planck constant.

Why the factorial?

⬤ Particles are indistinguishable ... but appear in different quantum states

Why Planck constant?

⬤ Has the correct dimension (Z must be dimensionless)

⬤ We get the same result for noninteracting quantum particles in a box

⬤ Fails if quantum effects are important (vide infra)

Integrals over positions and momenta are separated

Integrals over momenta can be evaluated: $\int \exp\left(-\dfrac{p_{1,x}^2/2m}{k_B T}\right) dp_{1,x} = \sqrt{2\pi k_B T m}$ After $3N$ integrations we get:

$$Z = \frac{Q}{N! \Lambda^{3N}}, \quad \text{de Broglie thermal wavelength:} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Λ = de Broglie wavelength at typical particle velocity at given T

$$\text{requirement:} \; \Lambda \ll \text{typical atom–atom separation} \approx (V/N)^{1/3}$$

Configurational integral:

$$Q = \int \exp[-\beta U(\vec{r}_1, \ldots, \vec{r}_N)] \, d\vec{r}_1 \ldots d\vec{r}_N$$

do not confuse:
U = internal energy
$U(\vec{r}_1, \ldots)$ = potential

Mean value of a **static** quantity (observable):

$$\langle X \rangle = \frac{1}{Q} \int X(\vec{r}_1, \ldots, \vec{r}_N) \exp[-\beta U(\vec{r}_1, \ldots, \vec{r}_N)] \, d\vec{r}_1 \ldots d\vec{r}_N$$

Example

a) Calculate Λ for helium at $T = 2$ K.

b) Compare to the typical distance of atoms in liquid helium (density 0.125 g/cm^3).
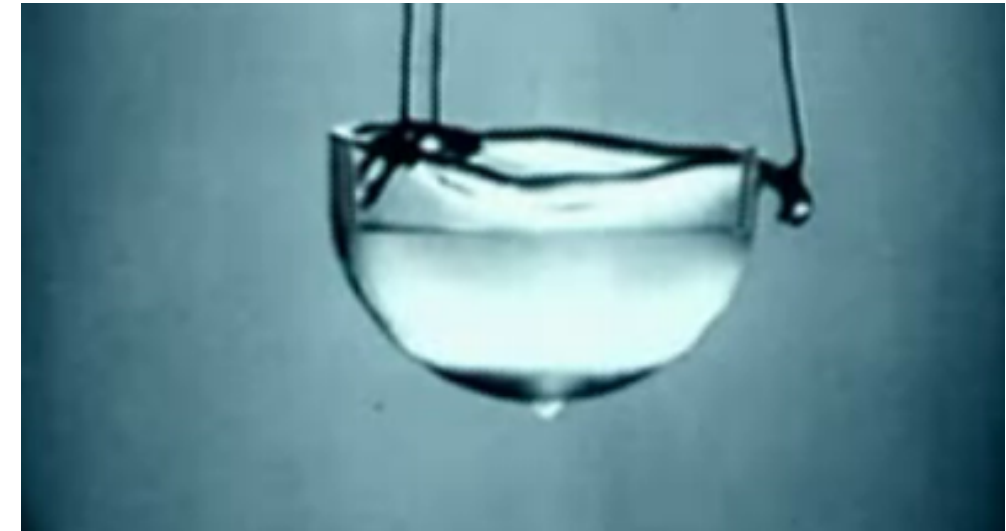
a) 6.2 Å; b) 3.8 Å

a)

$$\Lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B} T}}$$

$$= \frac{6.6 \times 10^{-34}}{\sqrt{2 \times \pi \times \frac{0.004}{6 \times 10^{23}} \times 1.38 \times 10^{-23} \times 2}}$$

$$= 6.2 \times 10^{-10}\,\mathrm{m}$$

credit: hight3ch.com/superfluid-liquid-helium/

b)

$$l = \sqrt[3]{V_1} = \sqrt[3]{\frac{M}{N_\mathrm{A}\rho}} = \sqrt[3]{\frac{0.004}{6 \times 10^{23} \times 125}} = 3.8 \times 10^{-10}\,\mathrm{m}$$

$l < \Lambda \Rightarrow$ cannot use classical mechanics

$$Q = \int \exp[0]\, d\vec{r}_1 \ldots d\vec{r}_N = \int_V d\vec{r}_1 \cdots \int_V d\vec{r}_N = V^N$$

$$Z = \frac{Q}{N!\Lambda^{3N}} = \frac{V^N}{N!\Lambda^{3N}} \approx \frac{V^N}{N^N e^{-N}\Lambda^{3N}}, \quad F = -k_B T \ln Z = -k_B T N \ln \frac{Ve}{N\Lambda^3}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_B T N}{V} = \frac{nRT}{V}$$

e = Euler number
e = elementary charge

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = \frac{3Nk_B T}{2}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_B T \ln\left(\frac{N\Lambda^3}{V}\right) = k_B T \ln\left(\frac{p\Lambda^3}{k_B T}\right)$$

(with respect to the standard state of a free molecule at zero temperature)

And verification:

$$G = F + pV = k_B T N \ln \frac{N\Lambda^3}{Ve} + Nk_B T = N\mu$$

Or quantum calculation of the translational partition function:

Eigenvalues of energy of a point mass in a $a \times b \times c$ box:

$$\mathcal{E} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Maxwell–Boltzmann statistics: high enough temperature so that a few particles compete for the same quantum state – it does not matter whether we have fermions or bosons; equivalently, $\Lambda \ll$ distance between particles.

Partition function:

$$Z_1 = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty}\exp(-\beta\mathcal{E}) \overset{\Sigma\to\int}{\approx} \int_0^{\infty}\int_0^{\infty}\int_0^{\infty}\exp(-\beta\mathcal{E})\,dn_x dn_y dn_z = \frac{V}{\Lambda^3}$$

$$E = \sum_{i=1}^{N} E_i \quad \Rightarrow \quad Z = \frac{1}{N!}Z_1^N$$

Yes, it is the same! The choice of factor $1/h^{3N}$ in the semiclassical Z was correct.